

# CHEMICAL AND ISOTOPIC STUDIES OF THE HGP-A GEOTHERMAL WELL

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The HGP-A well, located on the Lower East Rift Zone of Kilauea Volcano, was drilled in 1976. It is completed to a depth of 1966 m (1768 m below sea level) and has a bottom hole temperature of approximately 360°C. The well is capable of producing approximately 50,000 kg/hr of geothermal fluid (43% steam, 57% brine) at well-head pressure of 1172 kPa and is currently providing steam to a 3 megawatt electrical generator facility. During earlier testing periods and the present extended production (20 months as of the present date) from the well, a number of chemical and isotopic analyses have been conducted on the geothermal fluids discharged. The results of these analyses suggest that the geothermal system sampled by HGP-A is in some respects analogous to those observed at seafloor spreading centers such as Galapagos or the mid-Atlantic Ridge.

## Chemical Data

The major ion chemistry of the fluids produced by the HGP-A well at selected intervals is presented in Table 1. (The values presented are for total fluid chemistry after recombination of steam and brine fractions). Chloride ion concentration in geothermal fluids has been observed to increase throughout the production history of HGP-A; initial concentrations in the fluids were less than 1000 mg/kg, but with each production and during each production, chloride levels increased substantially.

Table 1. Chemical Composition of the HGP-A Reservoir Fluids (in mg/kg)

Date	Cl	Na	K	Mg	Ca	SiO <sub>2</sub>	ΣCO <sub>2</sub>	ΣH <sub>2</sub> S
11-8 -76	876	480	84.8	0.2	32.8	-	-	-
4-11-77	1220	584	106.4	0.1	30.9	404	-	-
6-12-81	637	322	61.6	0.021	7.4	480	600	450
9- 4-81	2109	1248	143	0.06	41.0	456	538	409
4-19-82	3017	1591	269	0.076	70.1	455	559	387
7-12-82	3445	1881	306	0.041	89.5	466	540	398
2-15-83	4260	2883	373	0.087	142.5	-	-	-
4-18-83	4392	2888	366	0.096	156.	467	538	412.8

The other major ion concentrations (Na, K, Ca, Mg) have also shown increases of varying magnitudes with time. If the source of saline fluids is seawater (as is discussed below), it is apparent that a major modification of the original fluid chemistry has occurred. The magnesium chloride ratios in the early production fluids indicate a strong depletion of magnesium ion relative to seawater ratios (RSWR); however, more recently there appears to have been a gradual increase in the Mg:Cl ratio with time. Similarly, calcium was initially depleted RSWR but has also shown an increase to the current condition where it is enriched by approximately 73% RSWR. The other major cations, sodium and potassium, were enriched by 7%-10% and by 300% respectively in the initial production fluids; these enrichments have remained relatively stable throughout the production history of the well.

Silica concentrations in the geothermal fluids have been somewhat variable and generally well below the concentrations anticipated for geothermal fluids in thermal equilibrium with reservoir rock at 360°C. It is of note that changes in the silica levels generally occur during initial well start-up but then stabilize to a nearly constant value of approximately 504 mg/kg at a fixed wellhead pressure of 1172 kPa. Similarly, the non-condensable gases carbon dioxide, hydrogen sulfide, nitrogen and hydrogen, have been present at nearly constant levels in the geothermal steam phase after initial excursions associated with well start-up.

#### Isotopic Data

During early production testing stable isotopic analyses were performed for hydrogen and oxygen; radio isotopic analyses of carbon dioxide and aqueous tritium were performed at this time as well. More recently a limited number of stable isotope analyses have also been conducted for reduced and oxidized sulfur species. Tritium ( $^3\text{H}$ ) and carbon-14 analyses have placed very broad limits on the age of the fluids present in the HGP-A reservoir; tritium data obtained after extended well flow tests have yielded values indicating an age of at least 50 years and tritium levels present after an extended pump-down test of modern water indicated that circulation within the reservoir in the immediate vicinity of the wellbore is on the order of at least years rather than months. Two carbon-14 analyses conducted on the well discharge several years apart yielded activities of approximately 20% of modern carbon indicating a maximum age of about 12,000 years. This age is considered to be an upper limit primarily because the contribution of magmatic carbon (of zero activity) to the total produced is currently unknown.

Stable isotope analyses of hydrogen and oxygen conducted on the early fluids produced by the well indicated that the source of the meteoric component of the reservoir fluids was from an altitude of a few thousand feet higher than that at which the well was located and that relatively little oxygen isotopic exchange had occurred between the reservoir rock and the geothermal fluids. It is highly probable that the fluids sampled for these analyses were heavily contaminated by surface water pumped into the well during quench operations; however, more recent analyses of these isotopes have not been performed to confirm this interpretation.

Sulfur isotopic analyses have been conducted on several samples of hydrogen sulfide (from the steam phase), aqueous sulfate, and pyrite and anhydrite collected from the HGP-A core samples. The results of these analyses are presented in Table 2. It is apparent that the sulfur isotopic ratios for the reduced and oxidized sulfur species are quite divergent suggesting that the reduced and oxidized species may have different sources. It is also noteworthy that there has been an apparent change in the hydrogen sulfide  $\delta^{34}\text{S}$  values with time.

Table 2. Ratios of Reduced and Oxidized Sulfur from HGP-A Well

Sample	$\delta^{34}\text{S}$	Sample	$\delta^{34}\text{S}$
$\text{H}_2\text{S}$ 6-12-81	+ 6.2	Sulfate 6-15-81	+ 20.4
$\text{H}_2\text{S}$ 6-25-81	+ 5.6	Sulfate 6-16-81	+ 21.5
$\text{H}_2\text{S}$ 7-22-81	+ 5.2	Sulfate 8- 3-81	+ 21.0
$\text{H}_2\text{S}$ 8- 3-81	+ 5.0	Anhydrite	+ 21.3
Pyrite	+ 1.8		

#### Discussion

Laboratory studies have found that the chloride ion concentration has been nearly constant during experimental alterations of basaltic minerals by seawater at high temperature (Mottl and Holland, 1978; Mottl et al., 1979; Seyfried and Bischoff, 1981). On this basis it is concluded that the source of the chloride present in the geothermal fluids sampled by HGP-A is seawater. The fact that the well is sampling fluids from a depth of at least 1000 m below any anticipated Gyhen-Herzberg fresh

water lens would suggest however that, in the absence of some form of hydrologic control in the area, the fluids in the geothermal reservoir should have a salinity equivalent to pure seawater rather than only 23% of seawater. It is suggested that the linear east-west trending system of dikes and fractures that forms the Kilauea Lower East Rift Zone provides a very effective structural control over the fluid flow paths within the rift zone and as a result seawater intrusion into the rift zone from the nearest point of access (ie from the south) is very effectively restrained. Deposition of anhydrite from the infiltrating seawater may also further serve to restrict fluid flow across the rift zone.

The small amount of seawater that has been able to infiltrate into the geothermal reservoir has been heavily altered by high temperature reactions with the reservoir rock. The nearly complete removal of magnesium from the saline fluids is due to the formation of the alteration mineral chlorite or possibly magnesium hydroxy sulfate ( $\text{Mg SO}_4 \times \text{Mg (OH)}_2 \cdot (1-2 \times \text{H}_2\text{O})$ ). Both minerals have been identified in laboratory seawater-basalt studies (Mottl and Holland, 1978; Seyfried and Bischoff, 1981; Bischoff and Rosenbauer, 1983) whereas only the former has been identified in the HGP-A cores.

The depletion of calcium ion in the early geothermal fluids was initially attributed to the precipitation of anhydrite from infiltrating seawater brought about by the increased temperatures in the rift zone. The depletion of sulfate and strontium ion concentrations in the fluids, and the presence of anhydrite in the HGP-A cores substantiate this mechanism. The recent increase in calcium ion suggests that more calcium is being liberated from alteration than can be consumed by the available sulfate. The mechanism for the change from calcium depletion to calcium enrichment is not well understood at the present time.

Potassium concentrations RSWR have remained enriched throughout the production history of HGP-A. Laboratory studies have indicated that potassium levels in seawater-basalt systems stabilize rapidly and, to a large extent, are controlled by the seawater to rock ratio (Mottl and Holland, 1978; Mottl et al., 1979). Comparison of the values observed in the HGP-A fluids with those obtained in laboratory studies conducted at similar temperatures (Mottl and Holland, 1978; Mottl et al., 1979; Seyfried and Bischoff, 1981) suggest that the water:rock ratio in the HGP-A reservoir may be in the range of 1 to 10.

The silica concentrations present in the geothermal fluids produced by the well are lower than expected for fluids in equilibrium with reservoir rock at a temperature of nearly 360°C. As noted above, the silica concentrations in the fluids peak during the initial surge of fluids from the well and then rapidly decline. The interpretation for this behavior is that the initial fluids reflect a near equilibrium concentration of silica within the immediate vicinity of the wellbore but, as the steam front moves out into the reservoir, the silica remaining in the fluids rapidly re-equilibrates to the lower brine temperatures brought about by steam loss.

The carbon dioxide present in the reservoir may be from several sources: seawater infiltration, meteoric recharge, and basaltic or magmatic carbon dioxide. The levels present are well within the range of those observed elsewhere however, they are above levels that would be expected from seawater and meteoric recharge alone. Laboratory studies conducted by Mottl and Holland (1978) indicate that the amounts of carbon provided by basaltic reactions are strongly dependant upon temperature at which alteration occurs and, on this basis, the  $\text{CO}_2$  concentrations observed in HGP-A fluids suggest that reservoir temperatures in the range of 400°C are possible.

The sources of sulfide in the reservoir are primarily basaltic or seawater sulfate reduction. Basalt-seawater studies (Mottl et al., 1979; Seyfried and Bischoff, 1981) have determined sulfide enrichments similar to those found in HGP-A at temperatures of 300°C to 400°C and rock-water ratios ranging from 1 to 10. The presence of pyrite and pyrrhotite in the cores and discharge fluids from the well indicate that these minerals may also be controlling the sulfide concentrations.

The radio-isotopic data from the geothermal fluids is useful only for a general evaluation of the age of the recharge water in the reservoir; approximately 80% of the carbon in the reservoir fluids could be from basaltic sources and hence carbon-14 age determined may correspond to recent carbon diluted by zero activity basaltic carbon. Nonetheless, a 12,000 year age for HGP-A reservoir fluids is considered to be young even without dilution by magmatic CO<sub>2</sub>.

The isotopic analyses of sulfur present in the geothermal fluids and cores suggest that the majority of the reduced sulfur is from basaltic sources whereas the sulfate is from seawater sources. However, fractionation studies conducted by Sakai (1968) indicate that these sulfate, pyrite and aqueous sulfide isotope ratios could reflect equilibrium ratios at 600°K under acid conditions in the reservoir. Hence, some portion of the reduced sulfide may be the result of sulfate reduction by iron minerals in the basalt rocks (the presence of hematite in the geothermal cuttings and cores would tend to support this interpretation) but the currently available sulfur isotope data does not require that this be the case.

### Conclusions

The data currently available regarding the fluid chemistry in the HGP-A well suggest several hypotheses regarding the chemical and hydrologic conditions in the geothermal system on the Kilauea East Rift Zone:

- 1) Structural constraints imposed on fluid flow by the Kilauea East Rift Zone control access of seawater into and across the geothermal reservoir.
- 2) The gradual increase in salinity of the geothermal fluids suggests that the HGP-A well is located near the southern boundary that isolates the rift zone from seawater intrusion.
- 3) The extreme alteration of the saline geothermal fluids indicates that the water-rock ratio in this portion of the rift zone is in the range of 1 to 10.
- 4) The apparent young age of the fluids produced by the reservoir, in conjunction with the low water rock ratio observed, suggests that this part of the reservoir has experienced intrusion of fresh basalt in the geologically recent past.

### References

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